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* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1](a) Under existence of a catalyst currently held on a carrier, at least one sort of compounds chosen from metal palladium, (b) heteropoly acid, and/or its salt, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process in a manufacturing method of a catalyst used for a manufacturing method of making [react by the gaseous phase]-ethylene and oxygen acetic acid.

A process of the 1st process catalyst support being impregnated in solution of a water-soluble

palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.
A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.
A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.
A process of supporting at least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and acquiring a catalyst for acetic acid manufacture.
[Claim 2](a) At least one sort of compounds and six group elements of (d) periodic table which were chosen from metal palladium, (b) heteropoly acid, and/or its salt, At least one sort of elements chosen from a group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements under existence of a catalyst currently held on a carrier, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process in a manufacturing method of a catalyst used for a manufacturing method of acetic acid to which ethylene and oxygen are made to react by the gaseous phase.
To the 1st process catalyst support, solution of a water-soluble palladium compound, and six group elements of (d) periodic table, A process of a solution of a compound containing at least one sort of elements chosen from a group which consists of seven group elements, eight group

elements, nine group elements, ten group elements, 11 group elements, and 12 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.
A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.
A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.
A process of supporting at least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and acquiring a catalyst for acetic acid manufacture.
[Claim 3](a) At least one sort of compounds and 14 group elements of (c) periodic table which were chosen from metal palladium, (b) heteropoly acid, and/or its salt, In a manufacturing method of a catalyst used for a manufacturing method of acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of a catalyst with which at least one sort of elements chosen from a group which consists of 15 group elements and 16 group elements are held on a carrier, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process.
A process of the 1st process catalyst support being impregnated in solution of a water-soluble palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.
A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make

palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.

A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

At least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, And a process of supporting a compound containing at least one sort of elements chosen from a group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, and acquiring a catalyst for acetic acid manufacture.

[Claim 4](a) At least one sort of compounds and 14 group elements of (c) periodic table which were chosen from metal palladium, (b) heteropoly acid, and/or its salt, At least one sort of elements and six group elements of (d) periodic table which were chosen from a group which consists of 15 group elements and 16 group elements, At least one sort of elements chosen from a group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements under existence of a catalyst currently held on a carrier, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process in a manufacturing method of a catalyst used for a manufacturing method of acetic acid

to which ethylene and oxygen are made to react by the gaseous phase.

To the 1st process catalyst support, solution of a water-soluble palladium compound, and six group elements of (d) periodic table, A process of a solution of a compound containing at least one sort of elements chosen from a group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.

A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

At least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, And a process of supporting a compound containing at least one sort of elements chosen from a group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, and acquiring a catalyst for acetic acid manufacture.

[Claim 5](a) At least one sort of compounds and 14 group elements of (c) periodic table which were chosen from metal palladium, (b) heteropoly acid, and/or its salt, In a manufacturing method of a catalyst used for a manufacturing method of acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of a catalyst with which at least one sort of

elements chosen from a group which consists of 15 group elements and 16 group elements are held on a carrier, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process.

A process of a solution of a compound containing at least one sort of elements chosen from a group which becomes the 1st process catalyst support from solution of a water-soluble palladium compound and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.

A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

A process of supporting at least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and acquiring a catalyst for acetic acid manufacture.

[Claim 6](a) At least one sort of compounds and 14 group elements of (c) periodic table which were chosen from metal palladium, (b) heteropoly acid, and/or its salt, At least one sort of elements and six group elements of (d) periodic table which were chosen from a group which consists of 15 group elements and 16 group elements, At least one sort of elements chosen from

a group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements under existence of a catalyst currently held on a carrier, A manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process in a manufacturing method of a catalyst used for a manufacturing method of acetic acid to which ethylene and oxygen are made to react by the gaseous phase.

To the 1st process catalyst support, solution of a water-soluble palladium compound, 14 group elements of (c) periodic table, A solution of a compound containing at least one sort of elements chosen from a group which consists of 15 group elements and 16 group elements, And a process of a solution of a compound containing at least one sort of elements chosen from a group which consists of six group elements of (d) periodic table, seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.

A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

A process of supporting at least one sort of compounds chosen as (a) metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and

acquiring a catalyst for acetic acid manufacture.

[Claim 7]A manufacturing method of the catalyst for acetic acid manufacture according to any one of claims 1 to 6, wherein barium salt is barium hydroxide.

[Claim 8]A manufacturing method of acetic acid making ethylene and oxygen react by the gaseous phase under existence of a catalyst for acetic acid manufacture acquired with the manufacturing method according to any one of claims 1 to 7.

[Claim 9]A manufacturing method of acetic acid making ethylene and oxygen react under existence of water by the gaseous phase under existence of a catalyst for acetic acid manufacture acquired with the manufacturing method according to any one of claims 1 to 7.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of acetic acid using the manufacturing method of a catalyst used when manufacturing acetic acid by an one-step catalytic reaction from ethylene and oxygen, and this catalyst.

[0002]

[Description of the Prior Art]Conventionally, as a manufacturing method of acetic acid, the oxidation style of acetaldehyde, the method to which methanol and carbon monoxide are made to react, the method of oxidizing low-grade paraffin, etc. are put in practical use.

[0003]On the other hand, since the method of manufacturing acetic acid from ethylene in one step has many advantageous points economically the industrial manufacturing process top, many proposals are made. For example, a 1 step of liquid phase oxidation style using oxidation reduction catalysts of the metal ion pair, such as palladium cobalt and iron (the France patent No. 1448361 gazette), the catalyst (JP,47-13221,A.) which consists of palladium phosphoric acid or a sulfur content denaturing agent The 1 step of gaseous phase oxidation style using JP,51-29425,A,

the catalyst (JP,54-57488,A) which consists of palladium salt of a certain kind of HETERIPORI acid, and the catalyst (JP,46-6763,A) which consists of a 3 formation oxygen compound, etc. are proposed.

[0004]Ethylene and the method (JP,7-89896,A, JP,9-67298,A) of compounding acetic acid by gaseous phase reaction from oxygen are proposed these days using the catalyst containing at least one sort of compounds chosen from metal palladium, heteropoly acid, and those salts. According to the method of using this catalyst, although acetic acid can be comparatively obtained with high yield, in manufacturing acetic acid on a scale of industrial, aging of the activity of a catalyst, i.e., the degradation of a catalyst, is important also for a small thing.

[0005]When carrying out performance of the method of compounding acetic acid by one step of gaseous phase from ethylene and oxygen using the catalyst containing at least one sort of compounds chosen from these metal palladium and heteropoly acid, and those salts on a scale of industrial, it is enough, but. The improvement in the further catalytic activity, especially reduction of the temporal degradation of a catalyst are called for.

[0006]

[Problem(s) to be Solved by the Invention]This invention according to the catalyst containing at least one sort of compounds chosen from metal palladium, heteropoly acid, and/or its salt. in the method of compounding acetic acid by gaseous phase 1 step reaction from ethylene and oxygen -- more -- high -- it aims at offer of the manufacturing method of an activity catalyst, especially the catalyst which reduced the degradation accompanying aging, and offer of the manufacturing method of acetic acid using this catalyst.

[0007]

[Means for Solving the Problem]So that this invention persons may improve performance of a catalyst containing at least one sort of compounds chosen from metal palladium used to achieve the above objects when compounding acetic acid by gaseous phase 1 step reaction from ethylene and oxygen, heteropoly acid, and/or its salt. It inquired wholeheartedly about a manufacturing method of the catalyst.

[0008]A catalyst containing at least one sort of compounds chosen from metal palladium, heteropoly acid, and/or its salt is the purpose of improving the dispersibility of these catalytic activity ingredient, and using, after having been supported by suitable carrier is usually preferred.

[0009]When manufacturing a carrier support type catalyst for acetic acid manufacture containing at least one sort of compounds chosen from metal palladium, heteropoly acid, and/or its salt, the following examples are given as the typical process, for example. That is, after a carrier is first impregnated in a solution of a palladium compound, reduction processing of palladium is performed using a suitable reducing agent, and a palladium metal carrier is obtained. Subsequently, heteropoly acid and/or its salt are supported to said palladium metal carrier, and a supported type catalyst for acetic acid manufacture is acquired to it.

[0010]In this process, after considering it as insoluble in water nature palladium by contacting a solution of a palladium compound to after-impregnating alkali in reduction processing of palladium, a method of carrying out reduction processing with a suitable reducing agent is effective. It is supposed that there is an effect which improves fully returning a palladium compound and the dispersibility of palladium metal particles to generate in this method. Conventionally, it is manufactured, using alkali, such as sodium hydroxide and metasilicic acid sodium, as an alkali treatment agent used for this alkali treatment.

[0011]Then, if this invention persons use barium salt solution as an alkali treatment agent as a result of repeating research wholeheartedly paying attention to an alkali treatment agent used for a process of obtaining metal palladium from this palladium compound, It finds out acquiring a catalyst which is high activity more and in which degradation by aging is smaller than a supported type catalyst for acetic acid manufacture prepared using an alkali treatment agent known conventionally, and came to complete this invention.

[0012]At least one sort of compounds which were chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt as for this invention (I) namely, under existence of a catalyst currently held on a carrier, In a manufacturing method of a catalyst used for a manufacturing method of acetic acid to which ethylene and oxygen are made to react by the gaseous phase, it is a manufacturing method of a catalyst for acetic acid manufacture, wherein a manufacturing process of this catalyst consists of the following process [1st] - the 4th process.

[0013]A process of the 1st process catalyst support being impregnated in solution of a water-soluble palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.

[0014]A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0015]A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

[0016]A process of supporting at least one sort of compounds chosen as a metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt.

[0017]At least one sort of compounds and 14 group elements of (c) periodic table in which this invention (II) was chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt, In a manufacturing method of a catalyst used for a manufacturing method of acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of a catalyst with which at least one sort of elements chosen from a group which consists of 15 group elements and 16 group elements are held on a carrier, A manufacturing process of this catalyst is a manufacturing method of a catalyst for acetic acid manufacture consisting of the following process [1st] - the 4th process.

[0018]A process of the 1st process catalyst support being impregnated in solution of a water-soluble palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.

[0019]A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0020]A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

[0021]At least one sort of compounds chosen as a metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, And a process of supporting a

compound containing at least one sort of elements chosen from a group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, and acquiring a catalyst for acetic acid manufacture.

[0022]At least one sort of compounds and 14 group elements of (c) periodic table in which this invention (III) was chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt, In a manufacturing method of a catalyst used for a manufacturing method of acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of a catalyst with which at least one sort of elements chosen from a group which consists of 15 group elements and 16 group elements are held on a carrier, A manufacturing process of this catalyst is a manufacturing method of a catalyst for acetic acid manufacture consisting of the following process [1st] - the 4th process.

[0023]A process of a solution of a compound containing at least one sort of elements chosen from a group which becomes the 1st process catalyst support from solution of a water-soluble palladium compound and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.

[0024]A process of making a solution of barium salt which can react to a water-soluble palladium compound an impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0025]A process of returning a palladium compound supported by impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a)

metal palladium carrier.

[0026]A process of supporting a compound containing at least one sort of compounds chosen as a metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and acquiring a catalyst for acetic acid manufacture.

[0027]In the 1st process of this invention (I) - this invention (III), this invention (IV) Six group elements of (d) periodic table, It is a manufacturing method of a catalyst for acetic acid manufacture by which a compound containing at least one sort of elements chosen from a group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements being impregnated.

[0028]This invention (V) is a manufacturing method of acetic acid making ethylene and oxygen react by the gaseous phase under existence of a catalyst for acetic acid manufacture manufactured with a manufacturing method of this invention (I) - (IV).

[0029]Hereafter, it explains in more detail about this invention.

[0030]

[Embodiment of the Invention]At least one sort of compounds chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt this invention (I) under existence of the catalyst currently held on the carrier, In the manufacturing method of a catalyst used for the manufacturing method of the acetic acid to which ethylene and oxygen are made to react by the gaseous phase, it is a manufacturing method of the catalyst for acetic acid manufacture, wherein the manufacturing process of this catalyst consists of the following process [1st] - the 4th process.

[0031]The process of the 1st process catalyst support being impregnated in the solution of a water-soluble palladium compound, and obtaining a water-soluble palladium compound

impregnating carrier.

[0032]The process of making the solution of the barium salt which can react to a water-soluble palladium compound the impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0033]The process of returning the palladium compound supported by the impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining a (a) metal palladium impregnating carrier.

[0034]The process of supporting at least one sort of compounds chosen as the metal palladium content carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt.

[0035]In this invention (I), there is no restriction in particular that what is necessary is just the porous material usually used as a carrier as catalyst support. Although silica, alumina, silica/alumina, diatomaceous earth, montmorillonite, or a titania is specifically mentioned, it is silica preferably.

[0036]There is no restriction in particular in the particle diameter of a carrier. They are 3 mm - 7 mm still more preferably 1 mm - 10 mm preferably. When circulating gas if particle diameter is too small in reacting to a tubular reactor by being filled up with a catalyst, big pressure loss arises and there is a possibility that the problem of gas stream Tooru becoming impossible etc. effectively may arise. On the other hand, when particle diameter is too large, there is a possibility that it may become impossible to diffuse reactant gas to the inside of a catalyst, and a catalyst component may stop working effectively.

[0037]There is no restriction in particular in the pore volume of a carrier, and specific surface area. as the pore volume of a carrier -- the range of 0.2 ml - 1.5 ml per gram -- good **** -- it is the range of 0.3 ml - 1.2 ml more preferably. As specific surface area of a carrier, the range of 10-m^2 per g of carrier - 800-m^2 is preferred, and is the range of 50-m^2 - 500-m^2 more preferably.

[0038]The palladium contained in the catalyst acquired in the catalyst manufacturing method of this invention (I) is metal palladium. The solution of a water-soluble palladium compound is impregnated with a carrier in the 1st process. As a palladium compound used here, if it is water solubility, there will be no restriction in particular. Specifically, a palladium chloride, tetra chloropalladium acid sodium and/or tetra chloropalladium acid potassium, a palladium nitrate, or sulfuric acid palladium is raised. Preferably, they are tetra chloropalladium acid sodium or a palladium nitrate.

[0039]There is no restriction in particular in the quantity of the palladium compound used in the 1st process. It is the quantity which serves as the range of 3g-18g as metal palladium per 1 l. of catalysts more preferably 1g - 20 g as metal palladium per 1 l. of catalysts in the catalyst for acetic acid manufacture acquired with the catalyst manufacturing method of this invention (I).

[0040]Although there is no restriction in particular in the quantity of the water used when a carrier is impregnated in a water-soluble palladium compound, it is 90% - 100% of range of the pore volume of catalyst support preferably. This figure can be set by measuring the water absorption of a carrier.

[0041]In the 2nd process, the carrier with which the solution of the water-soluble palladium compound was impregnated is added to the solution in which barium salt was dissolved. Under the present circumstances, a water-soluble palladium compound reacts to the barium salt which

is alkali, turns into an insoluble in water nature palladium compound, and deposits on a carrier.

[0042]Barium hydroxide is more preferred although there is no restriction in particular in the barium salt used at the 2nd process. An anhydride [$Ba(OH)_2$] or a hydrate may be sufficient as barium hydroxide. Although barium hydroxide and 8 hydrate [$Ba(OH)_2$ and $8H_2O$] is cheap and especially easy to come to hand, it does not limit to this.

[0043]The quantity of the barium salt to be used changes in proportion to the molar quantity of a water-soluble palladium compound and the absolute magnitude of acid of a carrier with which the carrier was impregnated. It is 1.0 Eq - 4.0 Eq preferably to the molar quantity of the water-soluble palladium compound with which the carrier was impregnated, and is the range of 1.2 Eq - 2.8 Eq more preferably.

[0044]A uniform thing is preferred, although barium salt solution may be uniform or it may be uneven. However, it may be uneven when you need the barium barium salt more than the solubility of the water to be used. Since the solubility to water increases while temperature goes up when using especially barium hydroxide, solution may be warmed, and it may be made a homogeneous solution and may use.

[0045]There is no restriction in particular in the water temperature at the time of adding the carrier with which the solution of the water-soluble palladium compound was impregnated to barium salt solution. Usually, although it is common to carry out at a room temperature, on an elevated temperature and a concrete target, you may warm more at 30 ** - about 50 **.

[0046]The contact time of barium salt solution changes with the water temperature at the time of processing, the kind of impregnating carrier, the quantity of the impregnated palladium, etc. It is the range of 18 hours - 30 hours more preferably for 12 hours or more. If contact time is too

short, there is a possibility that the water-soluble palladium with which the carrier was impregnated may change into insoluble in water nature palladium salt, and a deposit or immobilization of a up to [a carrier] may not fully be performed, and it is not desirable.

[0047]Subsequently, in the 3rd process, in order to return the insoluble in water nature palladium compound which deposited on the carrier to a metallic state, it processes with hydrazine, formaldehyde, ethylene, or a reducing agent like hydrogen.

[0048]Reduction processing may be performed in the state of any of the liquid phase and the gaseous phase, and if the condition is a general reducing condition, there will be no restriction in particular.

[0049]When performing reduction processing in the liquid phase, there is no restriction in particular in the temperature. Usually, although carried out at a room temperature, on an elevated temperature and a concrete target, you may warm more at 30 ** - about 50 **.

[0050]When performing reduction processing using a gaseous reducing agent in the gaseous phase, there is no restriction in particular in the temperature, but it is preferred to heat an impregnating carrier at 100 ** - around 300 **. If temperature is low, there is a possibility that the reduction to perfect palladium metal cannot be attained, and it is not desirable.

[0051]In the 4th process, at least one sort of compounds chosen as the metal palladium impregnating carrier obtained at the 3rd process from heteropoly acid and/or those salts are supported, and the catalyst for acetic acid manufacture is acquired.

[0052]There is no restriction in particular in the heteropoly acid used. As the hetero atom, are Lynn, silicon, boron, aluminum, germanium, cerium, cobalt, and chromium, and as a poly atom, What is necessary is just heteropoly acid containing at least one sort of elements chosen from

molybdenum, tungsten, vanadium, niobium, and tantalum.

[0053]Preferably as an example A tungstosilicic acid, phosphotungstic acid, Cay molybdic acid, molybdophosphoric acid, phosphorus molybdo tungstic acid, Cay molybdo tungstic acid, phosphorus BANADO tungstic acid, cay BANADO tungstic acid, cay BANADO molybdic acid, Howe tungstic acid, Howe molybdic acid, HOUMORIBUDO tungstic acid, etc. are mentioned. Especially, especially the heteropoly acid which a hetero atom becomes from Lynn or silicon, and at least one sort of elements chosen from the group which a poly atom becomes from tungsten, molybdenum, and vanadium is preferred.

[0054]The salt of heteropoly acid is metal salt or onium salt in which two or more sorts of inorganic oxacid replaced some or all of the hydrogen atom of acid that was condensed and generated. The metal which replaced the hydrogen atom of heteropoly acid is at least one sort of elements chosen from the group which consists of one fellows in the periodic table, two fellows, 11 fellows, and 13 fellows, and ammonium, ammonium salt with amines, etc. are illustrated as onium salt of heteropoly acid. Also in the salt of these heteropoly acid, especially metal salt of lithium, sodium, potassium, caesium, magnesium, barium, copper, gold, and gallium is preferred.

[0055]As a salt of a catalyst performance top and practically desirable heteropoly acid, although lithium salt of phosphotungstic acid, the sodium salt of phosphotungstic acid, the copper salt of phosphotungstic acid, the sodium salt of a tungstosilicic acid, and the copper salt of a tungstosilicic acid can be mentioned, It is not limited to these.

[0056]There is no restriction in particular in the support method to the carrier of heteropoly acid and/or its salt. After carrying out by what kind of method, dissolving in inorganic acid, such as suitable solvents and chlorides, such as water or acetone, nitric acid, and an acetic acid solution,

and organic acid and impregnating this in a carrier, supporting with the method of drying to a carrier is possible. Although means, such as the impregnating method, the evaporating method, the kneading method, and a spray method, are mentioned as an example, it is not limited to these.

[0057]In the catalyst for manufacturing-with manufacturing method of this invention (I) acetic acid manufacture, the composition ratio of at least one sort of compounds (a) chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt and (b), (a) 1 gram atom : (b)0.025 gramme molecule - 500 gramme molecules are preferred, and (a) 1 gram-atom:(b)0.1 - 400 gramme molecule is especially more preferred.

[0058]Although the holding amount of heteropoly acid to a carrier and/or its salt changes depending on the particle diameter and pore structure of a carrier, it is 10 % of the weight - 100% of the weight of a range preferably [that it is 5 % of the weight - 200% of the weight of within the limits to a carrier], and more preferably. Weight % to a carrier means here the value which broke the weight of heteropoly acid and/or its salt by weight of the carrier.

[0059]Next, the catalyst for acetic acid manufacture of this invention (II) is explained. At least one sort of compounds and 14 group elements of (c) periodic table in which this invention (II) was chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt, In the manufacturing method of a catalyst used for the manufacturing method of the acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of the catalyst with which at least one sort of elements chosen from the group which consists of 15 group elements and 16 group elements are held on the carrier, The manufacturing process of this catalyst is a manufacturing method of the catalyst for acetic acid manufacture consisting of the following process [1st] - the 4th process.

[0060]The process of the 1st process catalyst support being impregnated in the solution of a water-soluble palladium compound, and obtaining a water-soluble palladium compound impregnating carrier.

[0061]The process of making the solution of the barium salt which can react to a water-soluble palladium compound the impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0062]The process of returning the palladium compound supported by the impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

[0063]At least one sort of compounds and 14 group elements of (c) periodic table which were chosen as the metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, The process of supporting the compound containing at least one sort of elements chosen from the group which consists of 15 group elements and 16 group elements, and acquiring the catalyst for acetic acid manufacture.

[0064]The manufacturing method of the catalyst for acetic acid manufacture of this invention (I) of the 1st process of the manufacturing method of the catalyst for acetic acid manufacture of this invention (II), the 2nd process, and the 3rd process is the same, and the details are as above-mentioned.

[0065]Hereafter, the 4th process of this invention (II) is explained. The 4th process of this invention (II) is a process of supporting the compound containing at least one sort of elements chosen from the group which consists of at least one sort of compounds chosen from (b)

heteropoly acid and/or its salt and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, and acquiring the catalyst for acetic acid manufacture.

[0066]As at least one sort of compounds chosen from (a) metal palladium used for this invention (II) and (b) heteropoly acid, and/or those salts, it is the same as that of the raw material used for this invention (I). It is the same as that of this invention (I) also about a carrier.

[0067]14 group elements of (c) periodic table used by this invention (II), 15 group elements, and 16 group elements specifically refer to tin, lead, antimony, bismuth, selenium, a tellurium, etc. They are bismuth, selenium, and a tellurium preferably.

[0068]As an example of the compound containing at least one sort of elements which are used for manufacture of the catalyst of this invention (II), and which were chosen from the group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, a halogenide, a nitrate, acetate, etc. containing the element itself [this] or this element are mentioned. Specifically Tin chloride, acetic acid tin, a lead chloride, an antimony chloride, a bismuth chloride, Acetic acid tin, lead acetate, a lead nitrate, a selenium chloride, a selenium dioxide, selenic acid (H_2SeO_6), and its salts, Selenious acid (H_2SeO_3) and its salts, metal selenium, Although a tellurium, tellurium oxide, telluric acid (H_6TeO_6) and its salts, tellurous acid (H_2TeO_3) and its salts, a metal tellurium, etc. are mentioned, it is not limited to these.

[0069](b) There is no restriction in particular in the support method to the carrier of the compound containing at least one sort of elements chosen from the group which consists of at least one sort of compounds chosen from heteropoly acid and/or its salt and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements. After carrying out by what kind of method, dissolving in inorganic acid, such as suitable solvents and chlorides, such as water or

acetone, nitric acid, and an acetic acid solution, and organic acid and impregnating this in a carrier, supporting with the method of drying to a carrier is possible. Although means, such as the impregnating method, the evaporating method, the kneading method, and a spray method, are mentioned, it is not limited to these.

[0070]There is no restriction in particular in the order of the support to the carrier of the compound containing at least one sort of elements chosen from the group which consists of at least one sort of compounds chosen from (b) heteropoly acid and/or its salt and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements. After supporting (b) previously, (c) may be supported, or the reverse may be sufficient, and also (b) and (c) may be supported simultaneously.

[0071]At least one sort of compounds chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt in the catalyst for acetic acid manufacture manufactured with the manufacturing method of this invention (II), And the composition ratio of at least one sort of elements (a) chosen from the group which consists of 14 group elements of (c) periodic table, 15 group elements, and/or 16 group elements, (b), and (c), (a) 1 gram-atom: -- (b)0.025 gramme molecule - 500 gramme-molecule: -- (c)0.005 gram atom - 10 gram atom are preferred, and (a) 1 gram-atom:(b)0.1 gramme molecule - 400 gramme-molecule:(c)0.01 gram atom - 5 gram atom are especially more preferred.

[0072]Although the holding amount of heteropoly acid to a carrier and/or its salt changes depending on the particle diameter and pore structure of a carrier, it is 10 % of the weight - 100% of the weight of a range preferably [that it is 5 % of the weight - 200% of the weight of within the limits to a carrier], and more preferably. Weight % to a carrier means here the value which

broke the weight of heteropoly acid and/or its salt by weight of the carrier.

[0073]Next, the catalyst for acetic acid manufacture of this invention (III) is explained. At least one sort of compounds and 14 group elements of (c) periodic table in which this invention (III) was chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt, In the manufacturing method of a catalyst used for the manufacturing method of the acetic acid which makes ethylene and oxygen react by the gaseous phase under existence of the catalyst with which at least one sort of elements chosen from the group which consists of 15 group elements and 16 group elements are held on the carrier, The manufacturing process of this catalyst is a manufacturing method of the catalyst for acetic acid manufacture consisting of the following process [1st] - the 4th process.

[0074]The process of the solution of the compound containing at least one sort of elements chosen from the group which becomes the 1st process catalyst support from a water-soluble palladium compound and 14 group elements of (c) periodic table, 15 group elements, and 16 group elements being impregnated, and obtaining a water-soluble palladium compound impregnating carrier.

[0075]The process of making the solution of the barium salt which can react to a water-soluble palladium compound the impregnating carrier obtained at the 1st process of the 2nd process, and can make an insoluble in water nature palladium compound supporting on a carrier contacting, and obtaining an insoluble in water nature palladium compound impregnating carrier.

[0076]The process of returning the palladium compound supported by the impregnating carrier obtained at the 2nd process of the 3rd process to palladium metal with a reducing agent, and obtaining (a) metal palladium carrier.

[0077]The process of supporting the compound containing at least one sort of compounds chosen as the metal palladium carrier obtained at the 3rd process of the 4th process from (b) heteropoly acid and/or its salt, and acquiring the catalyst for acetic acid manufacture.

[0078]The manufacturing method of the catalyst for acetic acid manufacture of this invention (III), In the 1st process of the manufacturing method of the catalyst for acetic acid manufacture of this invention (I), water-soluble palladium salt and 14 group elements of (c) periodic table, A carrier is impregnated with the compound containing at least one sort of elements chosen from the group which consists of 15 group elements and 16 group elements, and other processes, i.e., the 2nd process, the 3rd process, and the 4th process are the same as that of this invention (I). There is no restriction in particular in the order which performs being impregnated with the compound containing at least one sort of elements chosen from the group which consists of water-soluble palladium salt, 14 group elements of (c) periodic table, 15 group elements, and 16 group elements. After water-soluble palladium salt is impregnated previously, (c) may be impregnated, or the reverse may be sufficient, and also water-soluble palladium salt and (c) may be impregnated simultaneously.

[0079]14 group elements of (c) periodic table used for this invention (III), 15 group elements, and 16 group elements specifically refer to tin, lead, antimony, bismuth, selenium, a tellurium, etc. They are bismuth, selenium, and a tellurium preferably.

[0080]As an example of the compound containing at least one sort of elements which are used for this invention (III), and which were chosen from the group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, a halogenide, a nitrate, acetate, etc. containing the element itself [this] or this element are mentioned. Specifically Tin

chloride, acetic acid tin, a lead chloride, an antimony chloride, a bismuth chloride, Acetic acid tin, lead acetate, a lead nitrate, a selenium chloride, a selenium dioxide, selenic acid (H_2SeO_6), and its salts, Selenious acid (H_2SeO_3) and its salts, metal selenium, Although a tellurium, tellurium oxide, telluric acid (H_6TeO_6) and its salts, tellurous acid (H_2TeO_3) and its salts, a metal tellurium, etc. are mentioned, it is not limited to these.

[0081]In the catalyst for acetic acid manufacture manufactured with the manufacturing method of this invention (III), (a) At least one sort of compounds chosen from metal palladium, (b) heteropoly acid, and/or its salt, And the composition ratio of (a), (b), and (c) of the catalyst containing at least one sort of elements chosen from the group which consists of 14 group elements of (c) periodic table, 15 group elements, and 16 group elements, (a) 1 gram-atom: -- (b)0.025 gramme molecule - 500 gramme-molecule: -- (c)0.005 gram atom - 10 gram atom are preferred, and (a) 1 gram-atom:(b)0.1 gramme molecule - 400 gramme-molecule:(c)0.01 gram atom - 5 gram atom are especially more preferred.

[0082]Although the holding amount of heteropoly acid to a carrier and/or its salt changes depending on the particle diameter and pore structure of a carrier, it is 10 % of the weight - 100% of the weight of a range preferably [that it is 5 % of the weight - 200% of the weight of within the limits to a carrier], and more preferably. Weight % to a carrier means here the value which broke the weight of heteropoly acid and/or its salt by weight of the carrier.

[0083]setting this invention (IV) to the manufacturing method of the catalyst for acetic acid manufacture of this invention (I) - (III) -- the time of the 1st process -- a water-soluble palladium compound -- or, With the compound containing at least one sort of elements chosen from the group which consists of a water-soluble palladium compound and 14 group elements of (c)

periodic table, 15 group elements, and 16 group elements. (d) It is a manufacturing method of the catalyst for acetic acid manufacture by which the compound containing at least one sort of elements chosen from the group which consists of six group elements of the periodic table, seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements being impregnated.

[0084]Six group elements of (d) periodic table used by this invention (IV), seven group elements, Specifically, at least one sort of elements chosen from the group which consists of eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements refer to elements, such as chromium, a rhenium, a ruthenium, rhodium, nickel, gold, and zinc. Chromium, gold, and zinc are raised suitably.

[0085]Six group elements of (d) periodic table used for manufacture of the catalyst of this invention (IV), As an example of the compound containing at least one sort of elements chosen from the group which consists of seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements, a halogenide, a nitrate, acetate, etc. containing the element itself [this] or this element are mentioned. Although nitrates, such as acetate, such as chloride salt, such as chromium chloride, ruthenium chloride, a rhodium chloride, chloroauric acid, and zinc chloride, chromium acetate, zinc acetate, and nickel acetate, chromium nitrate, zinc nitrate, and nickel nitrate, etc. are mentioned, specifically, it is not limited to these.

[0086]In the manufacturing method of this invention (IV), the solution of a water-soluble palladium compound, (c) The solution of the compound containing at least one sort of elements chosen from the group which consists of 14 group elements of the periodic table, 15 group

elements, and 16 group elements, And there is no restriction in particular in the turn of performing being impregnated to the carrier of the solution of the compound containing at least one sort of elements chosen from the group which consists of six group elements of (d) periodic table, seven group elements, eight group elements, nine group elements, ten group elements, 11 group elements, and 12 group elements, and it may carry out in what kind of turn. It may carry out independently, respectively and three ingredients may be performed simultaneously simultaneous in two arbitrary ingredients. (c) Or there is no restriction in particular in the support method to the carrier of (d). After carrying out by what kind of method, dissolving in inorganic acid, such as suitable solvents and chlorides, such as water or acetone, nitric acid, and an acetic acid solution, and organic acid and impregnating this in a carrier, supporting with the method of drying to a carrier is possible. Although means, such as the impregnating method, the evaporating method, the kneading method, and a spray method, are mentioned, it is not limited to these.

[0087]In the catalyst for acetic acid manufacture manufactured, with the manufacturing method of this invention (IV), (a) metal palladium, (b) At least one sort of compounds chosen from heteropoly acid and/or its salt, And six group elements of (d) periodic table, seven group elements, eight group elements, nine group elements, ten group elements, The composition ratio of (a), (b), and (d) in the case of the ternary system which consists of at least one sort of elements chosen from the group which consists of 11 group elements and 12 group elements, (a) 1 gram-atom: -- (b)0.025 gramme molecule - 500 gramme-molecule: -- (d)0.005 gram atom - 10 gram atom being preferred, and, especially -- (a) 1 gram-atom: -- (b)0.1 gramme molecule - 400 gramme-molecule: -- a more desirable result is given in (d)0.01 gram atom - 5 gram atom.

[0088]At least one sort of compounds chosen from (a) metal palladium, (b) heteropoly acid, and/or its salt, (c) At least one sort of elements chosen from the group which consists of 14 group elements of the periodic table, 15 group elements, and 16 group elements, And six group elements of (d) periodic table, seven group elements, eight group elements, nine group elements, ten group elements, The composition ratio of (a), (b), (c), and (d) in the case of the quaternary system which consists of at least one sort of elements chosen from the group which consists of 11 group elements and 12 group elements, (a) 1 gram-atom: -- (b)0.025 gramme molecule - 500 gramme-molecule: -- (c)0.005 gram atom - 10 gram-atom: -- (d)0.005 gram atom - 10 gram atom being preferred, and, especially -- (a) 1 gram-atom: -- (b)0.1 gramme molecule - 400 gramme-molecule: -- a more desirable result is given in (c)0.01 gram atom - 5 gram-atom (d)0.01 gram atom - 5 gram atom.

[0089]Although the holding amount of heteropoly acid to a carrier and/or its salt changes depending on the particle diameter and pore structure of a carrier, it is 10 % of the weight - 100% of the weight of a range preferably [that it is 5 % of the weight - 200% of the weight of within the limits to a carrier], and still more preferably. Weight % to a carrier means here the value which broke the weight of heteropoly acid and/or its salt by weight of the carrier.

[0090]Finally this invention (V) is explained. This invention (V) is a manufacturing method of ethylene and the acetic acid which compounds acetic acid by gaseous phase 1 step reaction from oxygen using the catalyst for acetic acid manufacture by a manufacturing method given in either this invention (I) - this invention (IV).

[0091]In the manufacturing method of acetic acid of this invention (V), oxygen is made to react to ethylene and there is no restriction in particular in the reaction temperature at the time of

manufacturing acetic acid. It is 100 ** - 300 ** preferably, and they are 120 ** - 250 ** still more preferably. Although it is advantageous practically that they are 0.0MPa (gage pressure) from a point of equipment - 3.0MPa (gage pressure) as for reaction pressure, there is no restriction in particular. It is the range of 0.1MPa (gage pressure) - 1.5MPa (gage pressure) more preferably.

[0092]manufacturing method **** of acetic acid of this invention (V) -- nitrogen, carbon dioxide, or rare gas can also be used for the gas supplied to the system of reaction as a diluent if needed including ethylene and oxygen.

[0093]To this distributed gas whole quantity, ethylene is 5 capacity % - 80 capacity %, and the quantity which 8 capacity % - 50 capacity % become comparatively preferably, and oxygen is 1 capacity % - 15 capacity %, and the quantity which 3 capacity % - 10 capacity % become comparatively preferably, and is supplied to the system of reaction.

[0094]In this system of reaction, when water is made to exist in the system of reaction, the improvement in acetic acid generation activity and selectivity and activity maintenance of a catalyst have an effect remarkably. Although it is preferred for a steam 1 capacity %-50 capacity % To be contained in reactant gas, they are 5 capacity % - 40 capacity % preferably.

[0095]In enforcing the manufacturing method of acetic acid of this invention (V), it is preferred to use the thing of a high grade as raw material ethylene, but even if lower saturated hydrocarbon, such as methane, ethane, and propane, mixes, it does not interfere. Although oxygen can be supplied by [what was diluted with inactive gas, such as nitrogen and carbon dioxide], for example, the form of air, when circulating reactant gas, generally it is [being high concentration and] more advantageous to use not less than 99% of oxygen suitably.

[0096]As for especially reaction mixed gas, in a normal condition, it is preferred space-velocity (SV)10Hr^{-1} - 10000Hr^{-1}, and to let it pass for a catalyst by 300Hr^{-1} - 5000Hr^{-1}.

[0097]As a reaction form, there is no restriction in particular and the form of a publicly known method, for example, the fixed bed, a fluid bed, etc. can be taken. It is advantageous practically to adopt the fixed bed which filled up with the above-mentioned catalyst preferably the coil which has corrosion resistance.

[0098]Although an example explains explanation for this invention still more concretely below, these examples show the outline of this invention and this invention is not limited to these examples.

[0099]

[Example][Example 1]

process (1): -- spherical silica carrier [which has 4 mm - 6 mm of impregnating particle diameters of palladium salt -- : by ZUDOHEMI -- kA-1] (69g) was impregnated to the solution (45 ml) of tetra chloropalladium acid sodium [product made from the Tanaka precious metals:Na_2PdCl_4] (3.8g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 2 minutes). The ****** carrier was settled at the room temperature after being impregnated for 1 hour.

[0100]Process (2):precipitate barium hydroxide 8 hydrate [-- Wako Pure Chem: -- the solution (100 ml) of $Ba(OH)_2$ and $8H_2O$] (8.4g) was quickly added to the ****** carrier obtained at the process (1), and the water-soluble palladium compound was changed into insoluble in water nature palladium. Churning rotation was carried out roughly and, subsequently the mixture was neglected calmly for 20 hours.

[0101]Process (3): The hydrazine 1 hydrate [Wako Pure Chem:N_2H_4andH_2O] solution (5 ml) was added to the mixture from a reducing process (2) 98%, and the insoluble in water nature palladium compound formed at the process (2) was changed into the metal of palladium by carrying out reducing agent processing. Subsequently, churning rotation was carried out calmly and, subsequently the mixture was settled for 20 hours.

[0102]The process (4) wash-water phase was decanted and removed, subsequently the output of the process (3) was washed 4 times with water (500 ml), and it decanted after washing. The acquired output was moved to the glass column with a stop cock, and subsequently, backwashing-by-water liquid rinsed further at speed of 1.5 l. per hour [about] until the chloride was lost by the silver nitrate test.

[0103]Process (5): The output from a drying process (4) was dried at 110 ** under air in oven for 4 hours, and, subsequently it was neglected in the desiccator overnight.

[0104]Process (6): The output acquired at the support process (5) of heteropoly acid or its salt was impregnated in the solution (45 ml) of the tungstosilicic-acid n hydrate (the product made from the NIPPON MUKI chemical industry: 20 to $H_4SiW_{12}O_{40}$ and nH_2O:n=30 hydrate) (24g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 3 minutes). The ****** carrier was settled at the room temperature after being impregnated for 1 hour. Subsequently, it dried at 110 ** under air in oven for 4 hours, and, subsequently was neglected in the desiccator overnight. This acquired the catalyst 1 for acetic acid manufacture.

[0105][Comparative example 1] Except having used metasilicic acid sodium 9 hydrate [Wako Pure Chem:$Na_2SiO_3$and$9H_2O$] (7.6g) instead of barium hydroxide 8 hydrate in the process (2) of

Example 1, it was manufactured by Example 1. This acquired the catalyst 2 for acetic acid manufacture.

[0106][Example 2] The process (1) - the process (5) were operated like Example 1, and performed the following operations henceforth [a process (6)].

[0107]Process (6) : Support of heteropoly acid or its salt, and periodic table 14 group element, 15 group elements. And the support process of 16 group elements. The output acquired by (5) was impregnated in the solution (45 ml) of a tungstosilicic-acid n hydrate (the product made from the NIPPON MUKI chemical industry: 20 to $H_4SiW_{12}O_{40}$ and nH_2O:n=30 hydrate) (24g), and telluric acid (0.30g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 3 minutes). The ****** carrier was settled at the room temperature after being impregnated for 1 hour. Subsequently, it dried at 110 ** under air in oven for 4 hours, and, subsequently was neglected in the desiccator overnight. This acquired the catalyst 3 for acetic acid manufacture.

[0108][Examples 3 and 4] In the process (6) of Example 2, instead of telluric acid, it was operated like Example 2 and the catalysts 4 and 5 for acetic acid manufacture were acquired except having used the compound given in Table 1.

[0109]

[Table 1]

実施例	触媒	化合物	添加量（g）
2	3	テルル酸	0．28
3	4	硝酸ビスマス	0．45
4	5	セレン酸	0．23

[0110][Comparative examples 2-4] In the process (2) of Example 2, metasilicic acid sodium 9 hydrate [Wako Pure Chem:Na_2SiO_3and9H_2O] (7.6g) is used instead of barium hydroxide 8 hydrate, Except having used the compound given in Table 2 in the process (6), it was manufactured by Example 2. This acquired the catalysts 6, 7, and 8 for acetic acid manufacture.

[0111]

[Table 2]

[0112][Example 5] The process (1) - the process (5) were operated like Example 1, and performed the following operations henceforth [a process (6)].

[0113]Process (6): The output acquired at the support process (5) of periodic table 14 group element, 15 group elements, and 16 group elements was impregnated in the solution of sodium telluride [Wako Pure Chem:Na_2TeO_3] (0.30g). The mixture was stirred until all the fluids were absorbed, and subsequently the catalyst was dried at 110 ** in oven for 4 hours.

[0114]Process (7): The output acquired at the support process (5) of heteropoly acid or its salt was impregnated in the solution (45 ml) of the tungstosilicic-acid n hydrate (the product made from the NIPPON MUKI chemical industry: 20 to $H_4SiW_{12}O_{40}$ and nH_2O:n=30 hydrate) (24g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 3 minutes). The ****** carrier was settled at the room

temperature after being impregnated for 1 hour. Subsequently, it dried at 110 ** under air in oven for 4 hours, and, subsequently was neglected in the desiccator overnight. This acquired the catalyst 9 for acetic acid manufacture.

[0115][Examples 6 and 7] In the process (6) of Example 5, instead of sodium telluride, it was operated like Example 5 and the catalysts 10-11 for acetic acid manufacture were acquired except having used the compound given in Table 3.

[0116]

[Table 3]

[0117][Comparative examples 5, 6, and 7] In the process (2) of Example 5, metasilicic acid sodium 9 hydrate [Wako Pure Chem:Na_2SiO_3and9H_2O] (7.6g) is used instead of barium hydroxide 8 hydrate, Except having used the compound given in Table 4 in the process (6), it was manufactured by Example 5. This acquired the catalysts 12, 13, and 14 for acetic acid manufacture.

[0118]

[Table 4]

[0119][Example 8]

process (1): -- spherical silica carrier [which has 4 mm - 6 mm of impregnating particle diameters of palladium salt -- : by ZUDOHEMI -- kA-1] (69g), tetra chloropalladium acid sodium [-- : made from the Tanaka precious metals -- Na_2PdCl_4] (3.8g) and zinc chloride [-- Wako Pure Chem: -- it was impregnated to the solution (45 ml) of $ZnCl_2$] (0.14g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 2 minutes). The ****** carrier was settled at the room temperature after being impregnated for 1 hour.

[0120]Process (2):precipitate barium hydroxide 8 hydrate [-- Wako Pure Chem: -- the solution (100 ml) of $Ba(OH)_2$ and $8H_2O$] (8.4g) was quickly added to the ****** carrier, and the water-soluble palladium compound was changed into insoluble in water nature palladium. Churning rotation was carried out roughly and, subsequently the mixture was neglected calmly for 20 hours.

[0121]Process (3): The hydrazine 1 hydrate [Wako Pure Chem:N_2H_4andH_2O] solution (5 ml) was added to the mixture from a reducing process (2) 98%, and the insoluble in water nature palladium compound formed at the process (2) was changed into the metal of palladium by carrying out reducing agent processing. Subsequently, churning rotation was carried out calmly

and, subsequently the mixture was settled for 20 hours.

[0122]The process (4) wash-water phase was decanted and removed, subsequently the output of the process (3) was washed 4 times with water (500 ml), and it decanted after washing. The acquired output was moved to the glass column with a stop cock, and subsequently, backwashing-by-water liquid rinsed further at speed of 1.5 l. per hour [about] until the chloride was lost by the silver nitrate test.

[0123]Process (5): The output from a drying process (4) was dried at 110 ** under air in oven for 4 hours, and, subsequently it was neglected in the desiccator overnight.

[0124]Process (6): The output acquired at the support process (5) of periodic table 14 group element, 15 group elements, and 16 group elements was impregnated in the solution of sodium telluride (0.23g) g. The mixture was stirred until all the fluids were absorbed, and subsequently the catalyst was dried at 110 ** in oven for 4 hours.

[0125]Process (7): The output acquired at the support process (5) of heteropoly acid or its salt was impregnated in the solution (45 ml) of the tungstosilicic-acid n hydrate (the product made from the NIPPON MUKI chemical industry: 20 to $H_4SiW_{12}O_{40}$ and nH_2O:n=30 hydrate) (24g). Addition is performed at once, and churning rotation of the mixture was calmly carried out until a solution was fully absorbed (for about 3 minutes). The ****** carrier was settled at the room temperature after being impregnated for 1 hour. Subsequently, it dried at 110 ** under air in oven for 4 hours, and, subsequently was neglected in the desiccator overnight. This acquired the catalyst 15 for acetic acid manufacture.

[0126][Examples 9 and 10] In the process (1) of Example 8, instead of zinc chloride, it was operated like Example 8 and the catalysts 16 and 17 for acetic acid manufacture were acquired

except having used the compound given in Table 5.

[0127]

[Table 5]

[0128][Comparative examples 8, 9, and 10] In the process (2) of Example 8, metasilicic acid sodium 9 hydrate [Wako Pure Chem:Na_2SiO_3and9H_2O] (7.6g) is used instead of barium hydroxide 8 hydrate, Except having used the compound given in Table 6 in the process (1), it was manufactured by Example 8. This acquired the catalysts 18, 19, and 20 for acetic acid manufacture.

[0129]

[Table 6]

[0130]Examples 11-20 : a catalytic activity test-method catalytic activity examination, The coil

made from SUS316 (25 mm in inside diameter) is filled up with 18.5 g of each catalyst for acetic acid manufacture, The capacity factor of ethylene, oxygen, water, and nitrogen reacted by introducing the gas supply mixed in proportion of 10:6:25:59 in space-velocity $^{-1}$ of 1800h by the reaction peak temperature of 200 ** of a catalyst bed, and reaction pressure 0.8MPa (gage pressure). The generated gas was cooled and gas chromatography (Shimazu Science, GC-14B, FID) analyzed the condensed reaction captured liquid.

[0131]The activity of the catalyst was calculated as a gram (space time yield, STY) of the acetic acid manufactured per catalyst liter per time, and the selectivity of the catalyst was calculated as percent of the conversion ethylene which exists in output.

[0132]A reaction result is shown in Table 7.

[0133]

[Table 7]

[0134][Comparative examples 11-20] The catalyst for acetic acid manufacture acquired in the comparative examples 1-10 was used, and also it reacted by the same method as Examples 11-20.

[0135]A reaction result is shown in Table 8.

[0136]

[Table 8]

[0137]

[Effect of the Invention]Although attained, manufacture of acetic acid from ethylene and oxygen The catalyst, i.e., (a) palladium metal, of this invention, And about manufacture of at least one sort of compounds chosen from (b) heteropoly acid and/or those salts, as compared with the conventional manufacturing method, are hard to be deactivated, therefore a catalyst with high productivity by the manufacturing process of a catalyst. It is obtained by precipitating an

insoluble in water nature palladium compound on catalyst support, using barium salt as a precipitant.

[Translation done.]